

# PATENT SPECIFICATION

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745,698



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## COMPLETE SPECIFICATION

### Improvements in or relating to methods of Producing Silicon of High Purity

We, STANDARD TELEPHONES AND CABLES LIMITED, a British Company, of Connaught House, 63, Aldwych, London, W.C.2, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the manufacture of a body of silicon.

It is well known to make rectifier devices using a body of silicon, but such devices have not proved entirely satisfactory and have been superseded to a very large extent by similar devices using germanium as the semi-conductor material, even though silicon is abundantly present in nature and germanium is a rare element.

It is also well known that the characteristics of rectifiers are affected to a very great extent by relatively small amounts of impurities present in the semi-conductor material. The difficulties experienced with silicon rectifiers are in large degree due to the difficulty of obtaining silicon with a controlled amount and kind of impurity. In order that silicon of this kind may be obtained, it is necessary first to obtain silicon of a high degree of purity.

Attempts have been made by various different processes to produce high purity silicon. Thus silicon stated to be hyper-pure has been prepared by the vapour phase reduction of silicon tetrachloride by means of zinc and later digesting the product with acids to purify the resultant silicon. Even this process when carried out with the greatest degree of care to avoid contamination of the product has been found by us not to produce silicon of sufficiently high purity to guarantee that the impurities were present to such a small extent as not to affect the electrical resistivity of the product.

It is accordingly an object of the present invention to provide a process of producing silicon which is capable of yielding silicon so pure that there is less than a spectrographic trace of any significant impurity.

In order to obtain pure silicon it is necessary to start with a silicon compound that can be obtained in a high degree of purity. Silane ( $\text{SiH}_4$ ) is such a compound.

The thermal decomposition of silane is known theoretically (see J.A.C.S., 1936, Vol. 58, p. 109) but the method has never been used commercially for the production of silicon.

It is the object of the present invention to produce substantially pure silicon on a commercial scale.

According to the present invention a process of manufacture of substantially pure silicon comprises the step of passing substantially pure silane in a molecular concentration substantially less than normal into a zone heated to the decomposition temperature of silane.

In this statement, "silane" means the compound  $\text{SiH}_4$ , only, and does not include any other hydride of silicon. By "molecular concentration substantially less than normal" is meant that the number of silane molecules per cubic centimetre is substantially less than the number present in one cubic centimetre of pure silane gas at atmospheric pressure, and at the decomposition temperature. The reduced molecular concentration may be obtained by storing the pure silane after generation, and then drawing it off under reduced pressure into the decomposition zone. Alternatively, the silane may be diluted with one of the inert gases such as argon, by which, for example, it may be swept into the decomposition zone from the vessel in which it is generated.

Since the decomposition is carried out by heat alone, there is no risk of contamination of the silicon by a chemical reagent. By means of

this process we have been able to obtain silicon of a higher degree of purity than any previously obtainable.

The decomposition of the silane generally produces the silicon in the form of dust, and for use for rectifiers or other purposes the dust must be converted into a solid body, and obviously great precautions must be taken to avoid contamination of silicon in processes used for such conversion.

The process of manufacture of silicon according to the present invention readily lends itself to the direct production of a coherent body of silicon by locating a seed of silicon in the decomposition zone. By reducing the molecular concentration of silane the number of molecules of silicon formed can be limited to the number that can fit into the growth of a coherent body at the temperature concerned. The seed of silicon is, in this method moved away from the decomposition zone at a rate which keeps the growing surface at substantially the same place.

It should be noted that silane may be decomposed by heat either by a heterogeneous (surface) reaction or by a homogeneous (gas phase) reaction. In depositing silicon by the decomposition of silane upon a silicon surface conditions must be such that only the surface reaction occurs. The streaming velocity of the gas at the growing surface, the pressure of the gas and the temperature of the surface are interdependent factors. Using argon as the inert gas to sweep the silane to the growing surface it is found that, even at a comparatively low temperature of 850°C for the growing surface i.e. a temperature below the melting point of silicon the streaming velocity of the gas was required to be between 100 and 150 litres per hour to prevent the gas phase decomposition, the molecular concentration of the silane being about 0.3 percent.

The same general considerations apply if the growing surface of the body of silicon be kept at the melting point of silicon. As the temperature of the growing surface is raised it is necessary to increase the flow rate of inert gas and decrease the flow rate of silane. This necessarily reduces the growth rate of silicon so that it is preferred to operate the process of growing a body of silicon by keeping the growing surface below the melting point and preferably not higher than about 800°C. The temperature must obviously exceed the decomposition temperature of silane, which is in the neighbourhood of 500°C.

Instead, however, of sweeping the silane from the vessel in which it is generated it is possible and in some ways preferred to store the silane in conventional types of gas storage cylinders and afterwards draw off the silane from such a cylinder into the decomposition zone. The considerations set out above as to ensuring decomposition only by a surface reaction also apply to this process and in order

to reduce the molecular concentration of the silane and to ensure the requisite flow at the growing surfaces for the purpose the silane is drawn into the decomposition zone under reduced pressure.

The invention will be better understood from the following description of two different embodiments thereof taken in conjunction with the accompanying drawings in which:

Fig. 1 is a flow sheet of a method of an embodiment of the invention,

Fig. 2 shows apparatus for drawing silane under reduced pressure into a decomposition zone in which it is deposited on the surface of a seed of silicone,

Fig. 3 shows the shape of a body of silicon produced by thermal decomposition of silane on a seed of silicon.

Referring to the drawing and first to Fig. 1, the reactants for producing silane are preferably silicon tetrachloride and lithium aluminium hydride. Silicon tetrachloride is purified, as indicated by step 1. Refluxing with copper turnings reduces the arsenic content from 1 milligram per millilitre to less than 0.01 micrograms per ml. All but very minute quantities of arsenic and other elements present in the form of chlorides are then removed by fractional distillation, the boiling points of the chlorides being fairly widely separated.

The silicon tetrachloride is mixed as indicated at 2 with pure dry ether or tetrahydrofuran which, as indicated at 3 has been purified by known methods of distillation and chemical treatment.

Lithium aluminium hydride is refluxed as indicated at 4 with dry ether or tetrahydrofuran thus eliminating volatile hydrides. The purified resulting solution or suspension of lithium aluminium hydride is reacted with the solution of silicon tetrachloride as indicated at 5, a stream of inert gas such as argon, previously purified, being first introduced as indicated at 6 to sweep out any air present in the reaction vessel.

It should here be noted that it is advisable that the whole of the apparatus used for the steps of the process hitherto specified should be made of quartz rather than glass since the materials used may pick up small amounts of undesirable impurities from glass.

The stream of carrier gas fed in as shown at 6 is continued in order to sweep the silane generated from the reaction vessel and the mixture of carrier gas and silane subjected as indicated at 7 to fractional freezing and fractional distillation in order still further to ensure purity of the silane.

The silane may then be passed into storage cylinders as indicated at 8 or may be passed without storage as indicated at 9 to the decomposition stage. The thermal decomposition stage 10 is always performed with less than normal concentration of the silane and this may be accomplished either by drawing the

silane from the storage stage 8 by reduced pressure as explained hereinafter or by reintroducing the purified carrier gas eliminated at stage 7 to sweep the silane into the decomposition zone.

The purified silane from stage 7 may still contain minute traces of other volatile hydrides. Silane is a very stable hydride as regards thermal decomposition and its decomposition temperature is higher than those of any hydrides of other elements that may still be present. In order to remove these traces of other hydrides the silane may be passed through a decomposition purification stage 11 in which hydrides of arsenic, boron and other possible significant impurities are decomposed. A small amount of silane may also be decomposed, the resulting silicon, arsenic, boron &c being thus removed.

The silane is decomposed at stage 10, preferably to deposit silicon on to a seed of silicon, hydrogen being produced and led off.

It should be noted that there are no corrosive resultants of the decomposition and thus the silicon produced is in a substantially pure state, indeed so pure that spectrographic analysis shows no measurable amount of impurities.

As stated above the conditions of molecular concentration and gas velocity immediately above the surface of the seed 10 are adjusted to secure decomposition of the silane only by a surface reaction.

Fig. 2 shows an example of apparatus used in a method of growing pure crystalline silicon from gaseous silane. The decomposition chamber 12 constituted by a cylinder 13 with end plates 14 and 15 sealed to the cylinder 13 in vacuum tight manner. A crystalline silicon seed 16 is fixed in a holder supported on a rod 17 and its upper surface heated by direct coupling to a copper current concentrator 18 which is water cooled by circulating water through a coiled tube 19, water entering at 20 and leaving at 21. The concentrator 18 forms the secondary winding of a radio frequency transformer the primary coil 22 of which forms a tuned circuit of an induction heater oscillating at a frequency of approximately 1 Mc/s.

Silane is admitted to the chamber 12 from a storage cylinder or from the fractional freezing and distillation step 7, Fig. 1, through an inlet 23 and 25 passes through a flow meter 24 and a valve 25 to an inlet pipe 26 which terminates just above an aperture 27 in the concentrator 18. The contour of the aperture 27 in proximity to the face of the silicon seed 16 is arranged to have a shape which will melt the upper surface of the seed 16 and give a solid-liquid interface of the required form.

The horizontal portion of the inlet pipe 26 passes through an induction heating coil 28 with a metallic core whereby the temperature within the core is raised to between 300° and

500°C. Any decomposition products form an adherent deposit on the walls of the tube 26.

The silane is drawn through the aperture 27 in the concentrator 18 by means of a vacuum pump connected to an outlet pipe 29, with the interposition of a pressure regulating tap 30.

The rod 17 passes through a vacuum seal 31 in the lower plate 15 and is connected to a mechanism 32 which rotates and lowers it at a predetermined rate.

The flow rate as read on the meter 24 and the pressure as read on a manometer 33 are adjusted by the valves 25 and 30 to give optimum crystal growth.

The rate at which the rod 17 is lowered is adjusted to be sufficient to keeping the surface of the seed or body 16, growing as it does with the addition of silicon, at the same level. The silicon in the growing body as it is lowered from this level gradually cools and crystallises.

If the seed 16 originally present is a monocrystal the growth takes place in monocrystalline form at the upper surface if the molecular concentration of the silane adjacent to the growing face be such as to ensure decomposition substantially wholly on the surface of the seed and substantially avoid a gaseous phase reaction. This can be secured by proper adjustment of the pressure in the chamber and the rate of flow in accordance with the temperature of the upper growing surface.

A certain amount of polycrystalline material is also formed on the outside of the monocrystal the appearance of the grown body being as shown in one section in Fig. 3. The original monocrystal is shown at 16. Monocrystalline growth builds up the extension 34 of the original monocrystal 16 whilst extraneous polycrystalline growth occurs as shown at 35. The portion 35 may be ground away if it is desired to use only the monocrystal.

On the other hand if a faster rate of growth is desired the original seed 16 may be polycrystalline and conditions adjusted for such faster rate of growth, for which however it is still advisable to secure only a surface decomposition. The polycrystalline body of silicon may then be converted into a monocrystal by the known method of melting and pulling a crystal from the melt.

While the principles of the invention have been described above in connection with specific embodiments, and particular modifications thereof, it is to be clearly understood that this description is made only by way of example and not as a limitation on the scope of the invention.

What we claim is:—

1. A process of manufacture of substantially pure silicon which comprises passing substantially pure silane in a molecular concentration substantially less than normal into a zone heated to a temperature at least equal to the decomposition temperature of silane.

2. A process of manufacture of substantially

pure silicon which comprises sweeping a stream of substantially pure silane by means of a substantially pure inert gas into a zone heated to a temperature at least equal to the decomposition temperature of silane.

3. A process of manufacture of substantially pure silicon which comprises drawing a stream of substantially pure silane by application of reduced pressure into a zone heated to a temperature at least equal to the decomposition temperature of silane.

4. A process of manufacture of a coherent body of substantially pure silicon which comprises flowing a stream of substantially pure silane, in a molecular concentration substantially less than normal, into a zone heated to a temperature at least equal to the decomposition temperature of silane and locating in said zone a seed of silicon upon which silicon from said silane is deposited.

5. A process of manufacture of a coherent body of silicon as claimed in Claim 4 comprising the further step of moving said seed away from said zone at such speed as to ensure that any surface of the growing body upon which silicon is deposited remains in said zone.

6. A process of manufacture of a coherent body of silicon as claimed in claim 4 in which the heating of said zone is accomplished by heating a surface of said seed to said temperature.

7. A process as claimed in claim 6 in which said surface is heated to such temperature that the silicon at said surface is molten.

8. A process of manufacture of a coherent body of substantially pure silicon which comprises flowing a stream of substantially pure silane on to the surface of a seed of silicon heated to a temperature above the decomposition temperature of silane and located in an enclosure and adjusting the rate of flow of said silane and the pressure in said enclosure to ensure decomposition of said silane substantially wholly upon the surface of said seed.

9. A process of manufacture of substantially pure silicon which comprises reacting a solution of substantially pure silicon tetrachloride with a liquid suspension of lithium aluminium hydride to produce substantially pure silane and subsequently introducing said silane in reduced molecular concentration into a zone heated to a temperature at least equal to the decomposition temperature of silane.

10. A process as claimed in claim 8 which comprises heating the surface of a seed of silicon to said temperature by induction heating whereby silicon produced by the decomposition of said silane is deposited on said seed.

ERNEST E. TOWLER,  
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For the Applicants.

#### PROVISIONAL SPECIFICATION

#### Improvements in or relating to methods of Producing Silicon of High Purity

WE, STANDARD TELEPHONES AND CABLES LIMITED, a British Company, of Connaught House, 63, Aldwych, London, W.C.2, England, do hereby declare this invention to be described in the following statement:—

This invention relates to a process for the manufacture of a body of silicon.

It is well known to make point contact rectifier devices using a body of silicon, but such devices have not proved entirely satisfactory and have been superseded to a very large extent by similar devices using germanium as the semi-conductor material, even though silicon is abundantly present in nature and germanium is a rare element.

It is also well known that the characteristics of point contact rectifiers are affected to a very great extent by relatively small amounts of impurities present in the semi-conductor material. The difficulties experienced with silicon rectifiers are in large degree due to the difficulty of obtaining silicon with a controlled amount and kind of impurity. In order that silicon of this kind may be obtained, it is necessary first to obtain silicon of a high degree of purity.

Attempts have been made by various differ-

ent processes to produce high purity silicon. Thus silicon stated to be hyper-pure has been prepared by the vapour-phase reduction of silicon tetrachloride by means of zinc and later digesting the product with acids to purify the resultant silicon. Even this process when carried out with the greatest degree of care to avoid contamination of the product has been found by us not to produce silicon of sufficiently high purity to guarantee that the impurities were present to such a small extent as not to affect the electrical resistivity of the product.

It is accordingly an object of the present invention to provide a process of producing silicon which is capable of yielding silicon so pure that there is less than a spectrographic trace of any significant impurity.

In order to obtain pure silicon it is necessary to start with a silicon compound that can be obtained in a high degree of purity. Silane ( $\text{SiH}_4$ ) is such a compound.

The thermal decomposition of silane is known theoretically (see J.A.C.S., 1936, Vol. 58, p. 109) but the method has never been used commercially for the production of silicon.

We have, however, found it possible to produce large quantities of silicon by the thermal decomposition of silane.

According to the present invention a process of manufacture of substantially pure silicon comprises the step of sweeping a stream of substantially pure silane by means of an inert gas through a zone heated to the decomposition temperature of silane.

Since the decomposition is carried out by heat alone there is no risk of contamination by a chemical reagent.

By means of this process we have been able to obtain silicon of a higher degree of purity than any previously obtainable.

The silicon is deposited in the form of dust and for use in rectifiers or other purposes the silicon dust thus produced must be converted into a solid body and obviously great precautions must be taken to avoid contamination of the silicon during any processes used for such conversion.

The process of manufacture of silicon according to the present invention readily lends itself to the direct production of a coherent body of silicon and according to a further feature of the present invention a process of manufacture of a coherent body of silicon comprises the steps of sweeping a stream of substantially pure silane by means of an inert gas through a zone heated to the decomposition temperature of silane and sweeping the silicon dust by a stream of inert gas downwards through a heated zone in which is located a solid body of silicon and heating the surface of said solid body of silicon presented to the said dust to a temperature above the melting point of silicon.

The process of producing the dust and the process of producing the solid body may be combined in one operation the silane gas being swept downwards through a thermal decomposition zone below which is located the molten surface of the body upon which the dust is deposited.

In this method of producing a coherent body of silicon the original body of silicon is lowered at a rate which keeps the growing surface substantially at the same place.

If the solid body of silicon originally present, on which the dust obtained by the decomposition of the silane is deposited, is a monocrystal of silicon the deposition of silicon thereon under the conditions stated above leads to the production of a single crystal of silicon.

An embodiment of the invention will now be described with reference to the accompanying drawing which shows diagrammatically an apparatus for carrying out the invention.

A suspension of lithium aluminium hydride in ether is prepared in a vessel 1. A stream of an inert gas such as argon, nitrogen or hydrogen is passed into the vessel 1 from an inlet pipe 2 through a tap 3 and the lower part 4 of a tap funnel and sweeps out any air in the vessel 1. After an interval a solution of silicon tetrachloride in ether contained in the upper part 5 of the tap funnel is allowed to flow into the vessel 1 by the opening of a tap 6.

Silane is generated in vessel 1 as a result of the reaction between the silicon tetrachloride and the lithium aluminium hydride and is swept by the inert gas through an outlet pipe 7 which passes downwards into a vessel 8 heated to a temperature above the decomposition temperature of silane. This heating is performed by the induction heating by a coil 9 of the upper surface of a body 10 of silicon supported on a vertical rod 11 passing upwards into the vessel 8. The upper surface of this body 10 is heated to a temperature above the melting point of silicon and radiates heat into the part of the vessel 8 immediately above it to an extent sufficient to cause decomposition of the silane.

The silicon resulting from this decomposition is deposited in the molten form on the surface of the body 10. The rod 11 is lowered at a rate sufficient to keep the surface of the body 10, growing as it does with the addition of silicon, at the same level. The silicon in the body 10 as it is lowered from this level gradually cools and crystallises and if the body 10 was initially a monocrystal the body grows as a single crystal of silicon.

The inert gas is led off by a tube 12.

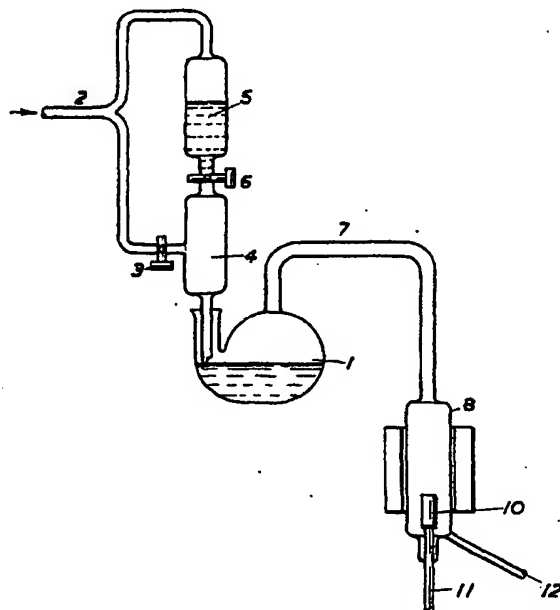
It is to be understood that the apparatus is provided with all necessary trap joints between the different portions thereof. All the enclosing walls and pipes shown should be made of silica of high purity. The silica of which the vessel 1 in particular is made and preferably also other vessels and tubes should be free of any boron or other material which may form a significant impurity in the silicon and so affect its conductivity in either direction of applied e.m.f.

ERNEST E. TOWLER,  
Chartered Patent Agent,  
For the Applicants.

# 745,698 PROVISIONAL SPECIFICATION

1 SHEET

*This drawing is a reproduction of the Original on a reduced scale.*



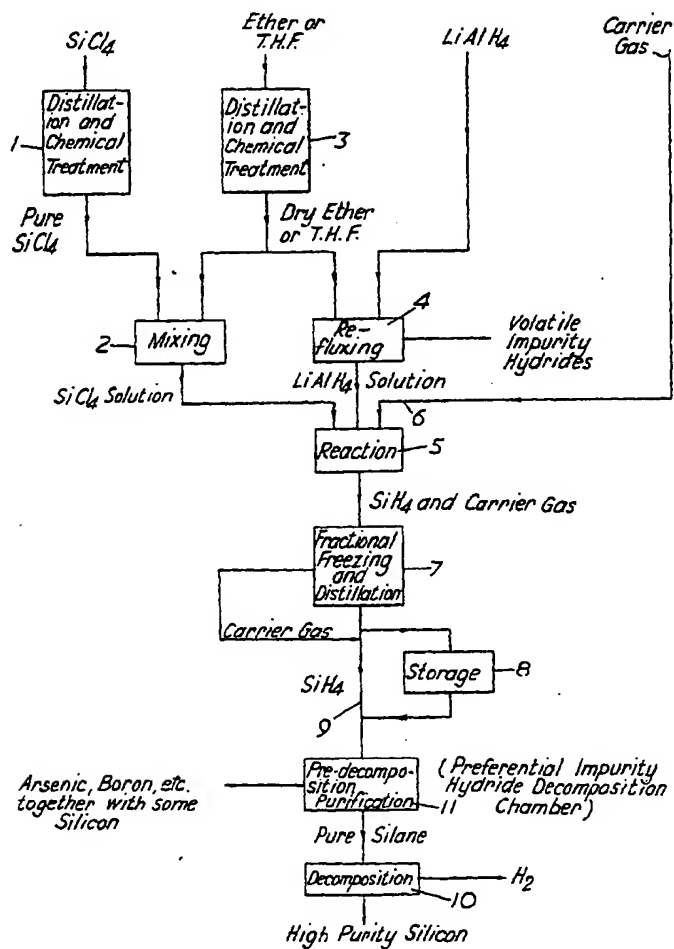


FIG. 1.

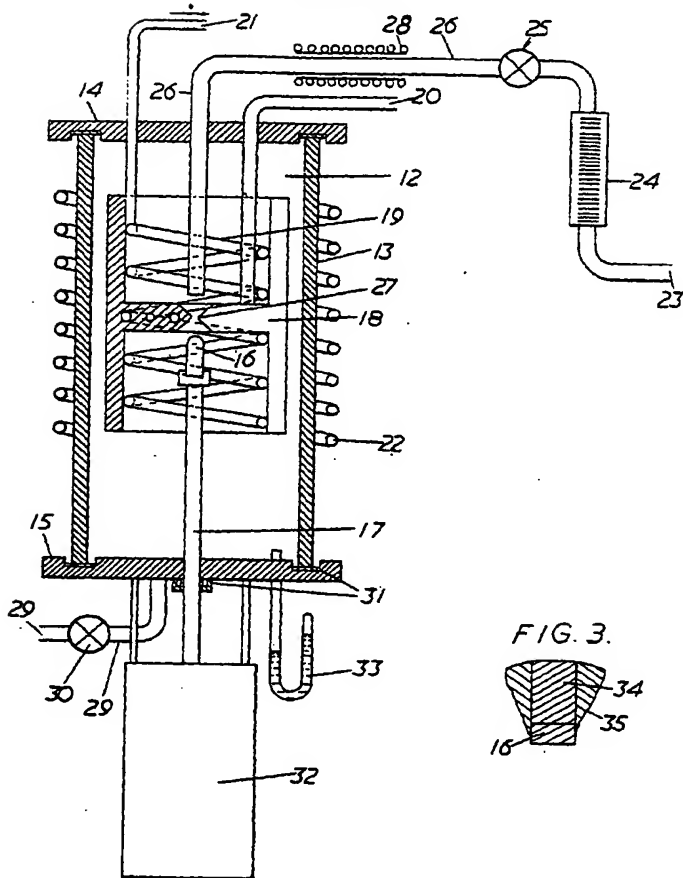
# 745698 COMPLETE SPECIFICATION

2 SHEETS

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the Original on a reduced scale.  
SHEETS 1 & 2

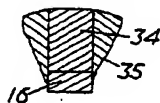
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FIG. 2.



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von

FIG. 3.





745698 COMPLETE SPECIFICATION  
The following is a specification of  
the invention as a reduced work  
SHEETS 1 & 2

